

Lineshape Theory and Photon Counting Statistics for Spectral Fluctuations in Quantum Dots : a Lévy Walk Process

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(February 1, 2008)

Recent experimental observations have found two different kinds of “strange kinetic behaviors” in individual semiconductor nanocrystals (or quantum dots). Fluorescence intermittency observed in the quantum dots shows power-law statistics in both *on* and *off* times. Spectral diffusion of the quantum dots is also described by power-law statistics in the sojourn times. Motivated by these experimental observations we consider two different but related problems: (a) a stochastic lineshape theory for the Kubo-Anderson oscillator whose frequency modulation follows power-law statistics and (b) photon counting statistics of quantum dots whose intensity fluctuation is characterized by power-law kinetics. In the first problem, we derive an analytical expression for the lineshape formula and find rich type of behaviors when compared with the standard theory. For example, new type of resonances and narrowing behavior have been found. We show that the lineshape is extremely sensitive to the way the system is prepared at time $t = 0$ and discuss the problem of stationarity. In the second problem, we use semiclassical photon counting statistics to characterize the fluctuation of the photon counts emitted from quantum dots. We show that the photon counting statistics problem can be mapped onto a Lévy walk process. We find unusually large fluctuations in the photon counts that have not been encountered previously. In particular, we show that Q may increase in time even in the long time limit.

I. INTRODUCTION

Recent studies have found fluorescence intermittency phenomena in single semiconductor nanocrystals (or quantum dots) such as CdSe illuminated under a continuous wave laser field [1–7]. In these experiments, a quantum dot (QD) typically exhibits blinking behavior; at random times the QD jumps between a bright state in which it emits many photons and a dark state in which it is “turned off” [1–7]. The *on* (or *off* state) is believed to correspond to a single electron-hole pair (or ionized) state of the QD [2]. Thus, the statistics of *on* and *off* times can tell us about the kinetic mechanisms of the QD blinking process.

In dramatic contrast to the usual expectation, distributions of *on* and *off* times of QDs follow a universal power-law behavior, not the characteristic, exponential behavior of Poissonian kinetics. It was found that the probability density functions (PDFs) of *on* and *off* times decay as $P_{\text{on}}(t_{\text{on}}) \propto 1/t_{\text{on}}^{m_{\text{on}}}$ and $P_{\text{off}}(t_{\text{off}}) \propto 1/t_{\text{off}}^{m_{\text{off}}}$, where $m_{\text{on}(\text{off})} \approx 3/2$ [4–7]. The *off* time distributions were measured over more than five decades in time, and seven decades in the PDF, $P_{\text{off}}(t_{\text{off}})$. [4–6]. This behavior appears universal; it is found in all individual QDs investigated, independent of the temperature, radius of the QD, and the laser intensity [4–6]. The *on* time distributions exhibit similar features. Although a secondary photo-induced mechanism introduces a cut-off time in the PDF of *on* times, the power-law behavior has still been observed in *on* time statistics over four decades in time and five decades in the PDF, $P_{\text{on}}(t_{\text{on}})$ [4–6]. The above mentioned cut-off time in the *on* time PDF depends on the laser intensity and the temperature, and when these effects become small, the cut-off time appears to diverge

(i. e., power-law behavior with no cut-off time). A single computational realization of the intensity fluctuation of the QD based on the two-state model is shown in Fig. 1.

The spectral diffusion process of the QD has also been investigated in other studies [8–10]. In these studies, the fluorescence emission spectrum of QDs was found to fluctuate between two central frequencies, for example, ω_+ and ω_- . The statistics of times, t_+ and t_- , during which a quantum dot emits photons at the frequency of ω_+ or ω_- was studied, and it was found that PDFs for t_+ and t_- follow the power-law behavior, $P_{\pm}(t_{\pm}) \propto 1/t_{\pm}^{m_{\pm}}$. Moreover, the exponents m_{\pm} are similar to those in the blinking statistics, $m_{\pm} \approx 3/2$ [10]. This suggests that there exists a strong correlation between fluorescence intermittency and spectral diffusion in QDs [9,10].

Standard approaches to lineshape phenomena and photon counting statistics are based on the Markovian assumption, and the spectral fluctuation is characterized by a finite, microscopic timescale. The statistics of t_{on} and t_{off} (or t_+ or t_-) observed in QDs clearly indicate the breakdown of standard assumptions made in conventional lineshape and photon counting statistics theories. The dynamical behaviors of the spectral diffusion process and the blinking process in QDs is non-Markovian, non-stationary, and non-ergodic. All these features are related to the fact that the average *on* and *off* times diverge, for example, $\langle t_{\text{off}} \rangle \propto \int_0^{\infty} dt t^{-3/2} t = \infty$. Hence, the dynamics of spectral diffusion and intermittency kinetics in QDs cannot be characterized by a microscopic timescale, which results in “strange” kinetics and leads to “strange” conclusions.

The $t^{-3/2}$ power-law behavior indicates that a simple random walk mechanism may be responsible for the observed behavior. Consider the following scenario: The

electron-hole pair generated in the QD under illumination is ionized via various mechanisms such as thermal [3] or Auger ionization [2] and the ionized electron or hole performs a certain kind of one-dimensional random walk either in a physical space such as on the surface of the QD, or in the energy space. Then, as is well known, the PDF of the first return time of the random walker to the origin follows the mentioned $3/2$ power-law behavior [11,12]. This PDF corresponds to the *off* time PDF. Similarly, the *on* time PDF will exhibit a $3/2$ power-law behavior when the ionization event is controlled by a one dimensional random walk mechanism. Shimizu *et al.* have suggested a resonant tunneling mechanism [6]. In this mechanism, the energy level of the ionized electron-hole pair in the QD in the dark state performs a one-dimensional random walk process, and when it matches a certain resonant condition, the tunneling process is facilitated so that it enables the recombination of the ionized electron-hole pair to occur, thus “turning on” the QD [6]. Alternatively, Kuno *et al.* have proposed a mechanism that attributes the power-law intermittency to fluctuations in the environment where QDs are located [5]. Local changes in the QD environments may cause the width and height of the tunneling barriers for the recombination of the electron-hole pair to fluctuate. If the Wentzel-Kramers-Brillouin-type theory for the tunneling process is considered, a minor fluctuation in the width or height of the tunneling barrier may result in a broad range of the tunneling times [5]. However, this does not explain the observed, universal $3/2$ power-law behavior. As far as we are aware, there is no definite physical picture of the exact nature of these processes.

Motivated by these observations, we consider in this paper two different but closely related phenomena characterized by the same power-law stochastic processes: lineshape theory with spectral diffusion process and photon counting statistics of fluorescence intermittency. As we demonstrate below, the lineshape for an ensemble of systems with a power-law spectral diffusion process such as QDs is completely different than that with the usual Poissonian case. An important issue in a power-law stochastic process is *stationarity*, which is of concern due to a very broad temporal distribution for underlying processes. We take into account the stationarity issue in the lineshape problem, and show that the lineshape is a very sensitive measure of stationarity when the underlying dynamics obeys power-law statistics.

In the second problem, we consider the photon counting statistics of QDs undergoing fluorescence intermittency characterized by the power-law process, and show that it exhibits unusually large fluctuations of photon number counts not encountered previously. We will show the relation between the statistics of photon emitted from QDs and Lévy walk processes that have been introduced in the context of continuous time random walks [13,14]. Lévy walk processes have been used to describe an enhanced diffusion (i.e., super-diffusion), and applied to many cases including a tracer diffusion in rotating flows

[15], models of deterministic chaotic diffusion [16] and of diffusion in random environments [17,18]. We predict that the photon counting statistics of an ensemble of these systems will exhibit large deviations from ordinary photon counting statistics. Specifically, Mandel’s Q parameter that measures the fluctuation of the photon counts will increase as the measurement time increases even in the long time limit.

II. LINESHAPE THEORY

Since its introduction by Kubo and Anderson (KA) [19,20] in the context of the lineshape theory, stochastic approaches to spectral lineshape theory have found wide applications in condensed phase spectroscopy ranging from magnetic resonance spectroscopy [19,20], nonlinear spectroscopy [21–24] to single molecule spectroscopy [25–29]. Analysis of lineshapes observed from an ensemble of molecules as well as from single molecules have revealed important dynamical information on the interaction between the chromophore and the environment. When molecules are embedded in a condensed media, the absorption frequency of the molecules changes in time due to the interaction between the molecules and the environment, which leads to a spectral diffusion process [21,30–33]. The influence of the spectral diffusion on the lineshape has been studied in many cases [8,21,25,27,34,35], and one of the well-known examples in these studies is the motional narrowing phenomenon: the linewidth decreases as the bath fluctuation rate increases. The motional narrowing phenomenon has been observed at the level of both the ensemble [36,21] and the single molecule [37]. In this section, we consider the Kubo-Anderson oscillator whose frequency undergoes spectral diffusion characterized by the power-law process as observed in recent studies of QDs [9,10], and calculate the lineshape of the oscillator.

A. Kubo-Anderson Oscillator Model

The stochastic lineshape theory of Kubo and Anderson is based on the equation of motion for the transition dipole [19,20,36],

$$\frac{d}{dt}\mu(t) = i\omega(t)\mu(t), \quad (2.1)$$

where $\omega(t)$ is the stochastic frequency of the oscillator. The dynamical quantity which determines the lineshape is the dipole correlation function or the relaxation function defined by

$$\Phi(t, t_0) = \langle \mu(t)\mu(t_0)^* \rangle, \quad (2.2)$$

where the average is taken over all the possible realizations of the underlying stochastic process and we have

set $\langle |\mu(t_0)|^2 \rangle = 1$. From the equation of motion we can calculate the relaxation function as

$$\Phi(t, t_0) = \left\langle \exp \left(i \int_{t_0}^t d\tau \omega(\tau) \right) \right\rangle. \quad (2.3)$$

When the process is assumed to be stationary, $\Phi(t, t_0) = \Phi(t - t_0)$, then the normalized *steady-state* lineshape $I(\omega)$ can be calculated as the Fourier transform of the relaxation function by making use of the Wiener-Khinchine(WK) theorem [38],

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \Phi(t) = \frac{1}{\pi} \text{Re} \hat{\Phi}(i\omega + \epsilon), \quad (2.4)$$

where the symmetry of $\Phi(t)$, $\Phi(-t) = \Phi^*(t)$, has been used, and $\epsilon \rightarrow 0^+$. The Laplace transform of $z(t)$ from t to s has been denoted by

$$\hat{z}(s) = \mathcal{L}\{z(t)\} = \int_0^{\infty} dt e^{-st} z(t). \quad (2.5)$$

To derive the lineshape formula given in Eq. (2.4) one can start, for example, from the optical Bloch equation governed by a stochastic Hamiltonian coupled to a monochromatic laser field and use a standard perturbation approximation for the field-matter interaction [39–41].

In calculating the average in Eq. (2.3), we assume that the underlying stochastic process is a renewal process as in the KA approach. To make the model as simple as possible, we only consider a two state model in this work. However, the current formulation can be extended into multi-state case. The transition frequency $\omega(t)$ of the chromophore can take the value of either ω_+ or ω_- depending on the perturber state, $+$ or $-$, respectively.

Each alternating path between the states $+$ and $-$ of the perturber leads to a stochastic realization of chromophore frequency modulation, and it is characterized by a sequence of sojourn times in the states $+$ and $-$. The sojourn times in the states \pm , t_{\pm} , are assumed as mutually independent, identically distributed random variables described by the probability density functions(PDFs), $\psi_{\pm}(t_{\pm})$. With the Markovian assumptions the original KA process amounts to the exponential sojourn time PDF,

$$\psi_{\pm}(t_{\pm}) = \frac{1}{\tau_{\pm}} \exp \left(-\frac{t_{\pm}}{\tau_{\pm}} \right). \quad (2.6)$$

We do not assume any specific functional forms for the sojourn time PDFs from the beginning, but are mainly interested in the process where the sojourn times are distributed with long time power-law tails, $t_{\pm}^{-(1+\alpha)}$ ($\alpha > 0$). Recent studies on the statistics of the spectral diffusion process in QDs correspond to the case $\alpha \approx 0.5$ [10].

B. Calculation of Lineshape

Unlike the Markovian, KA process, care should be taken in order to consider the stationarity of the non-Markovian stochastic processes described by the sojourn time PDF with non-exponential forms. When the stochastic process has been going on for long times before the beginning of the measurement at time $t = 0$, it is legitimate to assume that stationarity has been achieved in the process if $\langle t \rangle$ is finite.

We introduce $f_{\pm}(t)$, PDFs for times at which the oscillator makes the transition $\pm \rightarrow \mp$ *for the first time* after the beginning of the measurement, knowing that *the oscillator was at \pm at $t = 0$* , and these PDFs might be taken different from $\psi_{\pm}(t)$ in general. Following the physical argument given by Feller and others [42–45] (see also Appendix), the sojourn time PDFs for the *first* transition event after the measurement beginning at $t = 0$ are given by $f_{\pm}(t_{\pm})$ for the stationary case,

$$f_{\pm}(t_{\pm}) = \frac{1}{\tau_{\pm}} \int_{t_{\pm}}^{\infty} d\tau \psi_{\pm}(\tau), \quad (2.7)$$

where the mean sojourn times τ_{\pm} are given by

$$\tau_{\pm} = \int_0^{\infty} dt t \psi_{\pm}(t), \quad (2.8)$$

and they are assumed to be finite. This type of the initial condition is called *the equilibrium initial condition* [43], and they should be used in describing the stationary stochastic process. In this case, we have $\Phi(t, t_0) = \Phi(t - t_0)$, and we set $t_0 = 0$. When the mean sojourn time diverges, the concept of stationarity breaks down.

For the Poissonian case given in Eq. (2.6), we have $f_{\pm} = \psi_{\pm}$. Therefore, stationarity is naturally satisfied in the Poissonian process. However, the non-Poissonian process in which we are interested will not be stationary if we simply set $f_{\pm} = \psi_{\pm}$, and the WK theorem therefore does not hold in general. We note in passing that significant difference between stationary and nonstationary cases has manifested itself in many physical problems, e. g. transport properties in disordered materials [44] and power-spectra in chaotic systems [46].

The conditional relaxation functions $\Phi_{mn}(m, n = +, -)$ are defined over the stochastic paths that start from the state m at time 0 and end with the state n at time t ,

$$\Phi_{mn}(t) = \left\langle \exp \left(i \int_0^t d\tau \omega(\tau) \right) \right\rangle_{mn}, \quad (2.9)$$

and the total relaxation function is given in terms of Φ_{mn}

$$\Phi(t) = \sum_{m=\pm} \sum_{n=\pm} p_m \Phi_{mn}(t). \quad (2.10)$$

A sketch of the calculation of Φ_{mn} is given by using the convolution theorem of the Laplace transform [11].

For simplicity, we only consider in details the stochastic paths of the perturber that begin at the state + at time 0 and end at the state - at time t , thus contributing to Φ_{++} . Along a particular path if no transition is ever made until t , then the contribution of this path to Φ_{++} is given by $F_+(t_+)e^{i\omega_+t_+}$ in the time domain, where $F_\pm(t_\pm)$ are the probabilities that the first events $\pm \rightarrow \mp$ do not happen until time t and given by

$$F_\pm(t_\pm) = \int_{t_\pm}^{\infty} d\tau f_\pm(\tau). \quad (2.11)$$

This contribution will amount to $\hat{F}_+(s - i\omega_+)$ in the Laplace domain. The next possible paths are those which make the first transition to the state - at t_1 , jump back to the state + after remaining at the state - for time t_2 , and stay at the state + until time t . The contribution of these to $\Phi_{++}(t)$ is given by

$$\int_0^\infty dt_1 \int_0^\infty dt_2 \int_0^\infty dt_3 f_+(t_1) e^{i\omega_+t_1} \psi_-(t_2) e^{i\omega_-t_2} \Psi_+(t_3) e^{i\omega_+t_3} \quad (2.12)$$

with the constraint $t_1 + t_2 + t_3 = t$. Here, $\Psi_\pm(t_\pm)$ are the survival probabilities corresponding to $\psi_\pm(t_\pm)$, and defined by

$$\Psi_\pm(t_\pm) = \int_{t_\pm}^{\infty} d\tau \psi_\pm(\tau) = \tau_\pm f_\pm(t_\pm). \quad (2.13)$$

In the Laplace domain this contribution will read as

$$\hat{f}_+(s - i\omega_+) \hat{\psi}_-(s - i\omega_-) \hat{\Psi}_+(s - i\omega_+) \quad (2.14)$$

by the convolution theorem. Summing all the possible stochastic paths, we have

$$\begin{aligned} \hat{\Phi}_{++}(s) &= \hat{F}_+(s_+) + \hat{f}_+(s_+) \hat{\psi}_-(s_-) \\ &\quad \times [1 + \hat{\psi}_+(s_+) \hat{\psi}_-(s_-) + (\hat{\psi}_+(s_+) \hat{\psi}_-(s_-))^2 + \dots] \\ &\quad \times \hat{\Psi}_+(s_+) \\ &= \hat{F}_+(s_+) + \frac{\hat{f}_+(s_+) \hat{\psi}_-(s_-) \hat{\Psi}_+(s_+)}{1 - \hat{\psi}_+(s_+) \hat{\psi}_-(s_-)}, \end{aligned} \quad (2.15)$$

where $s_\pm = s - i\omega_\pm$. In a similar way, we have

$$\hat{\Phi}_{+-}(s) = \frac{\hat{f}_+(s_+) \hat{\Psi}_-(s_-)}{1 - \hat{\psi}_+(s_+) \hat{\psi}_-(s_-)}, \quad (2.16)$$

$$\hat{\Phi}_{--}(s) = \hat{F}_-(s_-) + \frac{\hat{f}_-(s_-) \hat{\psi}_+(s_+) \hat{\Psi}_-(s_-)}{1 - \hat{\psi}_+(s_+) \hat{\psi}_-(s_-)}, \quad (2.17)$$

$$\hat{\Phi}_{-+}(s) = \frac{\hat{f}_-(s_-) \hat{\Psi}_+(s_+)}{1 - \hat{\psi}_+(s_+) \hat{\psi}_-(s_-)}. \quad (2.18)$$

The total relaxation function can be calculated from the conditional relaxation functions,

$$\hat{\Phi}(s) = \sum_{m=\pm} \sum_{n=\pm} p_m \hat{\Phi}_{mn}(s), \quad (2.19)$$

with the initial distribution of the perturber state given by

$$p_\pm = \frac{\tau_\pm}{\tau_+ + \tau_-}. \quad (2.20)$$

Then from Eq. (2.4) the lineshape is given by

$$I(\omega) = \frac{1}{\pi} \text{Re} \left[\left(\frac{p_+}{z_+} + \frac{p_-}{z_-} \right) - \frac{1}{\tau_+ + \tau_-} \left(\frac{1}{z_+} - \frac{1}{z_-} \right)^2 \frac{(1 - \hat{\psi}_+)(1 - \hat{\psi}_-)}{1 - \hat{\psi}_+ \hat{\psi}_-} \right], \quad (2.21)$$

where $z_\pm = i\omega - i\omega_\pm$ and $\hat{\psi}_\pm = \hat{\psi}_\pm(z_\pm)$, and we have expressed all the sojourn time PDFs and survival probabilities in terms of $\hat{\psi}_\pm$,

$$\hat{\Psi}_\pm(s_\pm) = \frac{1 - \hat{\psi}_\pm(s_\pm)}{s_\pm}, \quad (2.22)$$

$$\hat{f}_\pm(s_\pm) = \frac{\hat{\Psi}_\pm(s_\pm)}{\tau_\pm}, \quad (2.23)$$

$$\hat{F}_\pm(s_\pm) = \frac{1 - \hat{f}_\pm(s_\pm)}{s_\pm}. \quad (2.24)$$

Eq. (2.21) is the final expression of the lineshape function for the stochastic oscillator undergoing the stationary two state frequency modulation.

It is our aim here to show that the lineshape theory exhibits a very *strong sensitivity* on the choice of PDF for the first event. This becomes important for experimental situations when it is not always clear if the underlying process is stationary or not. For this purpose we define a quasi-lineshape $\tilde{I}(\omega)$ by considering the following situation: In some experimental situations, a stochastic process undergoing in the system is not an on-going, stationary process, but it is initiated at a certain time, for example, $t = 0$. For this *nonstationary* case, we assume that the same sojourn time PDFs, ψ_\pm , describe the statistics of all the sojourn times, regardless of the first or the next sojourn times after $t = 0$. Then, a relaxation function $\tilde{\Phi}(t)$ can be defined as Eq. (2.3), $\tilde{\Phi}(t) \equiv \Phi(t, 0)$, with f_\pm replaced by ψ_\pm . The quasi-lineshape $\tilde{I}(\omega)$ is mathematically defined as a complex Laplace transform of $\tilde{\Phi}(t)$ in the same way as Eq. (2.4). It is obtained by replacing \hat{f}_\pm by $\hat{\psi}_\pm$ in the derivation of Eq. (2.21), which yields,

$$\begin{aligned} \tilde{I}(\omega) &= \frac{1}{\pi} \text{Re} \left[\frac{1}{1 - \hat{\psi}_+ \hat{\psi}_-} \left\{ p_+ \left(\frac{1 - \hat{\psi}_+}{z_+} + \frac{\hat{\psi}_+(1 - \hat{\psi}_-)}{z_-} \right) \right. \right. \\ &\quad \left. \left. + p_- \left(\frac{1 - \hat{\psi}_-}{z_-} + \frac{\hat{\psi}_-(1 - \hat{\psi}_+)}{z_+} \right) \right\} \right]. \end{aligned} \quad (2.25)$$

Note that for Poissonian case $\tilde{I}(\omega) = I(\omega)$. However, as we show here, a strong sensitivity on the first event is exhibited for power-law processes such that $I(\omega) \neq \tilde{I}(\omega)$.

We emphasize that $\tilde{I}(\omega)$ is not a lineshape obtained via the WK theorem. In general, the relaxation function, $\Phi(t_1, t_2)$, will depend on two-times for a nonstationary process, t_1 and t_2 , as given in Eq. (2.3), and the corresponding lineshape will be given by

$$I(\omega, T) \sim \frac{1}{T} \int_0^T dt_1 \int_0^T dt_2 e^{-i\omega(t_1-t_2)} \Phi(t_1, t_2), \quad (2.26)$$

which will depend on the total measurement time T . When the stationarity condition is satisfied, Eq. (2.26) is reduced to Eq. (2.4) in the limit $T \rightarrow \infty$ via the WK theorem [38].

C. Examples and Discussion

The original KA model is recovered from Eq. (2.21) by choosing an exponential sojourn time PDF [19,20]. We first consider the sojourn time PDFs which have finite first moments, $\tau_{\pm} < \infty$, but divergent second moments. As a representative of this class, we use the following form,

$$\psi_{3/2}(t; \tau) \equiv \left(\frac{\tau^3}{2\pi t^5} \right)^{1/2} \exp\left(-\frac{\tau}{2t}\right), \quad (2.27)$$

$$\psi_{\pm}(t_{\pm}) = \psi_{3/2}(t_{\pm}; \tau_{\pm}). \quad (2.28)$$

In this case, $\psi_{\pm}(t_{\pm})$ decays as $t_{\pm}^{-5/2}$ at long times, thus the first moment exists, but the second moment diverges.

In Fig. 2 we have compared $I(\omega)$ and $\tilde{I}(\omega)$ for $\psi_{\pm}(t)$ in Eq. (2.28) and for the KA case. For simplicity, we set the average frequency between ω_+ and ω_- as zero which amounts to a simple shift of the frequency origin, and define the magnitude of the frequency modulation as ω_0 ,

$$\frac{\omega_+ + \omega_-}{2} \Rightarrow 0, \quad (2.29)$$

$$\omega_0 \equiv \frac{\omega_+ - \omega_-}{2}. \quad (2.30)$$

We have chosen $\psi_+(t) = \psi_-(t) = \psi_{3/2}(t; \tau)$ in Eq. (2.28) by setting $\tau_+ = \tau_- = \tau$. The correlation time of the perturber dynamics is varied from slow ($\omega_0\tau \gg 1$) to fast ($\omega_0\tau \ll 1$) modulation cases in (a)-(d). For the KA case, the well known phenomenon of motional narrowing is shown: in the slow modulation case we see two peaks at $\omega = \pm\omega_0$ while in the fast modulation case we observe a single peak at $\omega = 0$. For the case of $\psi_{3/2}$, the stationary and nonstationary cases show very different behaviors as the correlation time is decreased; thus, the first event in the underlying random process has a strong effect on the lineshapes. In addition, new phenomena are found for the stationary lineshape in the fast modulation cases (Fig. 2(c) and (d)): three distinct peaks are observed for the stationary case.

The new peaks we observe in Fig. 2(c) and (d) at $\omega = \pm\omega_0$ for the stationary lineshape result from the

first event in the stochastic process $\omega(\tau)$. The probability for the perturber remaining at the initial state is governed by the long time tail in the sojourn time PDF. Due to the stationarity condition in Eq. (2.7) the survival probability for the first event decays more slowly for the stationary case ($\sim t^{1-\alpha}$) than for the nonstationary case ($\sim t^{-\alpha}$), where $\alpha = 3/2$ in this example. Therefore, the stationary case effectively requires the perturber to remain at the initial state until much longer times than the nonstationary case, resulting in the enhanced peaks at $\omega = \pm\omega_0$. This is why we observe new peaks not present in the standard Poissonian case.

As the next example, we consider the one-sided Lévy density as the sojourn time PDF [12],

$$\hat{\psi}(s) = \hat{L}_{\alpha}(rs) = \exp(-(rs)^{\alpha}), \quad (2.31)$$

with $0 < \alpha < 1$, and r being a coefficient with a time dimension. It is well known that the Lévy PDF in Eq. (2.31) decays algebraically at long times $t/r \gg 1$, $L_{\alpha}(t/r) \sim t^{-(1+\alpha)}$, and thus all the moments of $L_{\alpha}(t/r)$ including the first moment diverge [12]. Therefore, there is no microscopic timescale for this PDF, and the form of $f_{\pm}(t)$ given in Eq. (2.7) cannot be applied. However, in realistic situations, the power-law statistics is modified at long times to various reasons, for example, lifetime of a molecule. Therefore, it is natural to introduce a cut-off time t_c such that the algebraic decay is valid during time interval $r \ll t \ll t_c$. We introduce an exponential cut-off function for the convenience of an analytical treatment. Now the sojourn time PDFs are given by

$$\psi_{\pm}(t) = \mathcal{N}_{\pm} e^{-t/t_c} L_{\alpha}(t/r_{\pm}), \quad (2.32)$$

where \mathcal{N}_{\pm} are the proper normalization constants depending on the cut-off time. Then the Laplace domain expressions of $\psi_{\pm}(t)$ can be written as

$$\hat{\psi}_{\pm}(s) = \exp \left[\left(\frac{r_{\pm}}{t_c} \right)^{\alpha} \{1 - (1 + st_c)^{\alpha}\} \right]. \quad (2.33)$$

Then $f_{\pm}(t)$ are given from Eq. (2.7) with the mean given by

$$\tau_{\pm} = \alpha t_c \left(\frac{r_{\pm}}{t_c} \right)^{\alpha}. \quad (2.34)$$

Note that in the limit $t_c \rightarrow \infty$ the Lévy PDF without cut-off is recovered as $\hat{\psi}_{\pm}(s) = \exp(-(r_{\pm}s)^{\alpha})$ and τ_{\pm} diverge.

In Fig. 3 we have investigated the effect of the cut-off time in the Lévy PDF case both in the stationary and the nonstationary cases. When $\alpha = 0.3$ [Figs. 3 (a) and (b)], both the stationary and the nonstationary Lévy lineshapes show distinct peaks at $\omega = \pm\omega_0$. As the cut-off time is increased, lineshapes become narrower. When $\alpha = 0.8$ [Figs. 3 (c) and (d)], there appears a peak near $\omega = 0$ not present in $\alpha = 0.3$ case in Figs. 3 (a) and (b) in addition to two resonance peaks. This is a new

type of the narrowing behavior in that it is controlled by the power-law index α rather than the correlation time τ (as in the Poissonian case), and is termed *power-law narrowing* behavior. Also, as the cut-off time is increased, the central peak in the lineshape for the stationary case diminishes while it remains in the nonstationary case. This is because in the stationary case, as the cut-off time is increased the first event will dominate the probability weight in the stochastic paths of the perturber dynamics. The difference between the stationary and nonstationary cases is therefore more significant in the Lévy case than in the case $\psi_{3/2}(t)$ given in Fig. 1.

To investigate the power-law narrowing behavior we consider the limit $t_c \rightarrow \infty$. In this limit the stationary lineshape approaches two delta functions,

$$I(\omega) = p_+ \delta(\omega + \omega_0) + p_- \delta(\omega - \omega_0), \quad (2.35)$$

since the second term in the Eq. (2.21) vanishes as $\tau_{\pm} \rightarrow \infty$. The nonstationary case, however, yields in the limit $|\omega| r_{\pm} \ll 1$,

$$\lim_{t_c \rightarrow \infty} \tilde{I}(\omega) = \begin{cases} \frac{\sin(\pi\alpha)}{2\pi\omega_0} \frac{2+x+x^{-1}}{\eta x^{\alpha} + (\eta x^{\alpha})^{-1} + 2\cos(\pi\alpha)} & |\omega| < \omega_0 \\ 0 & |\omega| > \omega_0 \end{cases}. \quad (2.36)$$

This expression has been obtained from Eq. (2.25) by taking the small frequency limit of the sojourn time PDF,

$$\hat{\psi}_{\pm}(s) = 1 - A_{\pm} s^{\alpha} + \dots, \quad s \rightarrow 0 \quad (2.37)$$

where $A_{\pm} = r_{\pm}^{\alpha}$. Note that Eq. (2.36) is not limited to Lévy PDF, but valid for any PDF with $t^{-(1+\alpha)}$ tail ($0 < \alpha < 1$). Here, a dimensionless frequency, x , is defined by

$$x = \frac{\omega_0 + \omega}{\omega_0 - \omega}, \quad (2.38)$$

and an asymmetry parameter, η , by

$$\eta = \lim_{t_c \rightarrow \infty} \frac{p_+}{p_-} = \lim_{t_c \rightarrow \infty} \frac{\tau_+}{\tau_-} = \frac{A_+}{A_-}. \quad (2.39)$$

Eq. (2.36) shows very asymmetric power-law singularities, $\tilde{I}(\omega) \sim 1/(\omega_0 \pm \omega)^{1-\alpha}$ when $|\omega| \leq \omega_0$ depending on α . It is worthwhile to mention that such a strong asymmetric lineshape has been encountered in the problem of the X-ray edge absorption of metals [47].

In the symmetric case ($\eta = 1$) Eq. (2.36) reduces to a simpler expression,

$$\lim_{t_c \rightarrow \infty} \tilde{I}(\omega) = \frac{\sin(\pi\alpha)}{2\pi\omega_0} \frac{2+x+x^{-1}}{x^{\alpha} + x^{-\alpha} + 2\cos(\pi\alpha)}, \quad |\omega| < \omega_0 \quad (2.40)$$

and zero when $|\omega| > \omega_0$. In this case there exists a critical value of α below which the lineshape is concave and above which convex at $\omega = 0$, which is given by

$$\alpha_c = \cos(\pi\alpha_c/2) \Rightarrow \alpha_c = 0.594611\dots \quad (2.41)$$

We also note that in a recent study of the statistics of persistent events that models spin flips separated by random time intervals described by the Lévy law it has been shown that the distribution of the mean magnetization is described by an expression similar to Eq. (2.36) for the symmetric case, that is, $\eta = 1$ in Eq. (2.40) [48,49].

To confirm this finding we have plotted the stationary and nonstationary lineshapes for the Lévy PDF in Fig. 4 for the symmetric case ($\eta = 1$) as α is changed. Since we have chosen a very large but finite value of $t_c (= 10^4)$ the stationary lineshape still shows the central peak depending on the value of α , although it will approach two delta functions as $t_c \rightarrow \infty$. The nonstationary case in Fig. 4 (b) shows the concave-to-convex transition at the critical value of α as predicted. For the stationary lineshape, similar kind of behavior can be observed in Fig. 4 (a), however, α_c now depends on t_c .

III. PHOTON COUNTING STATISTICS

Photon counting statistics has proved useful for investigating dynamical processes of an ensemble of molecules as well as of single molecules in condensed phases [50,28,29]. In a semiclassical theory of photon counting statistics, when there is no source of fluctuation in the dynamics of chromophores other than shot noise due to the discrete nature of photons, the counting statistics of the photons emitted from the chromophores is characterized as Poissonian [50,28,29], and deviation of the photon counting statistics from the Poisson case indicates the characteristic of fluctuations. For example, a super-Poissonian, photon bunching phenomenon has been observed in many systems with various physical origins [30,32,51–53]. Recently, photon counting statistics for a single molecule that undergoes the KA spectral diffusion process characterized by Markovian, rate processes has been considered [28,29]. In this section, we consider the photon counting statistics of QDs undergoing the fluorescence intermittency characterized by the power-law process, and will show that unusual behavior in the photon counts is obtained.

A. Model for QD Fluorescence Intermittency

We assume a two state model for the fluorescence intensity fluctuation of the QD: $I(t) = I_+$ or $I(t) = I_-$. In the experiments mentioned in the introduction the state $+$ is the *on* state while the state $-$ is the *off* state and then $I_- = 0$. We consider a more general model where I_- is not necessarily equal to zero, corresponding to a single emitter jumping between two different emitting states that has been observed in other situations [54]. The $+$

and $-$ times are assumed to be mutually independent, identically distributed random variables. The PDFs of the \pm times is $\psi_{\pm}(t_{\pm})$.

We consider an ensemble of N , independent, statistically identical QDs undergoing such a random process. Let $P(n, t)$ be the probability of detecting n photon counts in the time interval $(0, t)$ from the sample. We use Mandel's semi-classical photon counting formula [50, 28, 29]

$$P(n, t) = \frac{W^n}{n!} \exp(-W), \quad (3.1)$$

where W is the macroscopic fluorescence intensity of the sample observed during the measurement time t

$$W = \sum_{n=1}^N w_n = \xi \sum_{n=1}^N \int_0^t dt' I_n(t'). \quad (3.2)$$

Here, w_n is the contribution of the n th QD to the total photon counts and obtained from the fluorescence intensity $I_n(t)$ of the n th QD. ξ is a coefficient which depends on the detection efficiency, and for simplicity, we set $\xi = 1$ without any loss of generality.

In the photon counting statistics of the ensemble, we need to consider two different averages: (i) average over the shot noise process due to the discreteness of photons, which is denoted by $\overline{(\cdots)} = \sum_{n=0}^{\infty} (\cdots) P(n, t)$, and (ii) average over the stochastic process the ensemble is undergoing, that is, random $I(t)$, which is denoted by $\langle \cdots \rangle = \int_0^{\infty} dW (\cdots) P(W, t)$, where $P(W, t)$ is the PDF of the random variable W . If $I_n(t)$ is non-random and independent of time, $I_n(t) = I$, the photon statistics is Poissonian with the mean $\bar{n} = W = NIt$. Averaged over the stochastic process, Eq. (3.1) can be written as

$$\langle P(n, t) \rangle = \int_0^{\infty} dW P(W, t) \frac{W^n}{n!} \exp(-W). \quad (3.3)$$

We see that $\langle P(n, t) \rangle$ is the Poisson transform of $P(W, t)$, which in principle can be calculated from the statistical properties of the stochastic process $I(t)$. To characterize the fluctuations, we use the Q parameter introduced by Mandel [50, 28, 29],

$$Q \equiv \frac{\overline{\langle n^2 \rangle} - \langle \bar{n} \rangle^2}{\langle \bar{n} \rangle} - 1, \quad (3.4)$$

Using Eq. (3.1) it is easy to show [50, 29]

$$\bar{n} = W, \quad (3.5)$$

$$\overline{\langle n^2 \rangle} - \bar{n} = W^2, \quad (3.6)$$

By using the fact that all QDs are statistically equivalent, we have

$$\langle \bar{n} \rangle = \langle W \rangle = N \langle w \rangle, \quad (3.7)$$

$$\overline{\langle n^2 \rangle} - \langle \bar{n} \rangle = \langle W^2 \rangle = N \langle w^2 \rangle + N(N-1) \langle w \rangle^2, \quad (3.8)$$

where we have dropped indices n in $\langle w_n \rangle$ and $\langle w_n^2 \rangle$ noting that they are independent of n . Then Q parameter becomes

$$Q = \frac{\langle w^2 \rangle - \langle w \rangle^2}{\langle w \rangle}. \quad (3.9)$$

We see that $Q \geq 0$ indicating a super-Poissonian behavior. When $Q = 0$ photon counting statistics is Poissonian.

The problem at hand is related to the Lévy walk model. Briefly, the Lévy walk model considers a test particle whose velocity switches randomly between two states v_{\pm} , and the sojourn times of these two states are assumed mutually independent, identically distributed random variables. The PDF of sojourn times is assumed to decay as a power-law. In our context we may identify I_{\pm} with the velocities of the Lévy walker, and w is its coordinate. We note that there are a few variants of the Lévy walk model (i.e., jump model, velocity model, and two state model) [16]. Our model maps onto the two state model considered first by Masoliver *et al.* [55]. There are two technical differences between the problem at hand and the previous work: in our case the random walk is biased and asymmetric.

B. Calculation of Q Parameter

As shown in the previous subsection, the calculation of Q parameter is reduced to the calculation of the fluctuation of the random variable w since the all QDs are statistically equivalent. We now consider the PDF and the characteristic function of w , $P(w, t)$ and $P(k, t)$, which are related to each other by the Fourier transform,

$$P(k, t) = \left\langle \exp \left(ik \int_0^t dt I(t) \right) \right\rangle = \int_{-\infty}^{\infty} dw \exp(ikw) P(w, t). \quad (3.10)$$

with $P(w < 0, t) = 0$. We note that the characteristic function $P(k, t)$ is mathematically equivalent to the relaxation function $\Phi(t)$ considered in the previous section, and therefore, can be calculated in the same way as before. One technical difference is that in the lineshape problem we have assured that the stationarity be guaranteed by using the equilibrium initial condition, Eq. (2.7), that involves different forms for the sojourn time PDFs corresponding to the first transition events. Here, we use the same sojourn time PDFs for all transition events, not distinguishing between the first steps and the others. Thus, the process is non-stationary.

The characteristic function is written as a sum of four terms in the same way as in Eq. (2.19),

$$P(k, t) = \sum_{m=\pm} \sum_{n=\pm} p_m P_{mn}(k, t) \quad (3.11)$$

where p_m is the probability that the process begins from the state m , and $p_+ + p_- = 1$. In Eq. (3.11), $P_{mn}(k, t) = \langle e^{ikw} \rangle_{mn}$ is the conditional characteristic function which is obtained by an average over paths restricted to the state m at the initial time 0 and the state n at final observation time t . It can be calculated via the same route taken for the calculation of the conditional relaxation function,

$$P_{++}(k, t) = \mathcal{L}^{-1} \left\{ \frac{1 - \hat{\psi}_+(s_+)}{s_+ [1 - \hat{\psi}_+(s_+) \hat{\psi}_-(s_-)]} \right\}, \quad (3.12)$$

$$P_{--}(k, t) = \mathcal{L}^{-1} \left\{ \frac{1 - \hat{\psi}_-(s_-)}{s_- [1 - \hat{\psi}_+(s_+) \hat{\psi}_-(s_-)]} \right\}, \quad (3.13)$$

$$P_{+-}(k, t) = \mathcal{L}^{-1} \left\{ \frac{\hat{\psi}_+(s_+) [1 - \hat{\psi}_-(s_-)]}{s_- [1 - \hat{\psi}_+(s_+) \hat{\psi}_-(s_-)]} \right\}, \quad (3.14)$$

$$P_{-+}(k, t) = \mathcal{L}^{-1} \left\{ \frac{\hat{\psi}_-(s_-) [1 - \hat{\psi}_+(s_+)]}{s_+ [1 - \hat{\psi}_+(s_+) \hat{\psi}_-(s_-)]} \right\}, \quad (3.15)$$

where $s_{\pm} = s - ikI_{\pm}$, and \mathcal{L}^{-1} is the inverse Laplace transform from s to t . The equivalence between the characteristic function of the random photon counts w in Eq. (3.12)-(3.15) and the relaxation function of the Kubo-Anderson oscillator in Eq. (2.15)-(2.18) can be seen explicitly if the correspondence between I_{\pm} and ω_{\pm} is recognized between two models, $I_{\pm} \leftrightarrow \omega_{\pm}$, and $f_{\pm} = \psi_{\pm}$ are used in Eq. (2.15)-(2.18).

Now, we consider the case where $\psi_+(t)$ and $\psi_-(t)$ decay for long times as $t^{-(1+\alpha)}$ with $0 < \alpha < 1$. The *on-off* intermittency of QDs corresponds to $\alpha = 1/2$ if $m_{\text{on}} = m_{\text{off}} = 3/2$. In what follows, we use the Tauberian theorem of the Laplace transform [11] to find the long time behavior of $\langle w \rangle$ and the fluctuation $\langle w^2 \rangle - \langle w \rangle^2$. We use the Laplace transforms of the sojourn time PDFs in the long time limit,

$$\hat{\psi}_{\pm}(s) = 1 - A_{\pm} s^{\alpha} + \dots, \quad s \rightarrow 0, \quad (3.16)$$

which means $\psi_{\pm}(t) \propto t^{-(1+\alpha)}$ for long times. Note that these sojourn time PDFs have diverging first and second moments. The initial conditions we choose are: $p_{\pm} = A_{\pm}/(A_{+} + A_{-})$.

To calculate $\langle w \rangle$ and $\langle w^2 \rangle$, we use

$$\langle w \rangle = -i \left. \frac{d \langle \exp(ikw) \rangle}{dk} \right|_{k=0}, \quad (3.17)$$

$$\langle w^2 \rangle = - \left. \frac{d^2 \langle \exp(ikw) \rangle}{dk^2} \right|_{k=0}. \quad (3.18)$$

Using Eq. (3.12)-(3.15) we find (for $0 < \alpha < 1$)

$$\langle w \rangle \sim (p_+ I_+ + p_- I_-) t. \quad (3.19)$$

The fluctuations are given by

$$\langle w^2 \rangle - \langle w \rangle^2 \sim (1 - \alpha) p_+ p_- (I_+ - I_-)^2 t^2. \quad (3.20)$$

We note that within the context of Lévy walks the behavior in Eq. (3.20) is called ballistic transport since the fluctuation $\langle w^2 \rangle - \langle w \rangle^2$ exhibits ballistic behavior ($\propto t^2$) instead of the normal Gaussian, diffusive behavior ($\propto t$).

As a second example, we consider two equal sojourn time PDFs which have finite first moments, $\langle t_{\text{on}} \rangle = \langle t_{\text{off}} \rangle = \tau$, but diverging second moments,

$$\hat{\psi}_{\pm}(s) = \hat{\psi}_{\mp}(s) = 1 - \tau s + A s^{\alpha} + \dots, \quad s \rightarrow 0 \quad (3.21)$$

with $1 < \alpha < 2$ and $p_+ = p_- = 1/2$. In this case we find in the long time limit,

$$\langle w \rangle \sim \left(\frac{I_+ + I_-}{2} \right) t, \quad (3.22)$$

for the fluctuations we find super-diffusive behavior,

$$\langle w^2 \rangle - \langle w \rangle^2 \sim \frac{A(\alpha - 1)(I_+ - I_-)^2}{2\tau\Gamma(4 - \alpha)} t^{3-\alpha}, \quad (3.23)$$

where $\Gamma(x)$ is the Gamma function. When $\alpha \rightarrow 2$ the fluctuations tend to become linear in time (for $\alpha = 2$, Lévy walks exhibit logarithmic corrections to the diffusive behavior). One can show that if $\alpha > 2$, namely, the case when the first two moments of the \pm times are finite, the fluctuation grows linearly with time.

C. Discussion

The photon statistics we find exhibits behavior which is very different than standard photon counting statistics. Specifically, Mandel's Q parameter may increase with measurement time even for long times. Using Eqs. (3.9), (3.19), (3.20), (3.22), and (3.23), we have

$$Q \propto \begin{cases} t & 0 < \alpha < 1 \\ t^{2-\alpha} & 1 < \alpha < 2 \\ t^0 & 2 < \alpha \end{cases} \quad (3.24)$$

This is in contrast to ordinary theories of photon counting statistics which predict $Q \rightarrow t^0$ [50,56]. From Eq. (3.24) we see that the fluctuations are extremely large if compared with the standard case corresponding to $\alpha > 2$. The mean of photon counts always increases as $\langle n \rangle \sim t$. Thus, it is Q not $\langle n \rangle$ that yields insight into the underlying “strange” kinetics.

The time-independent ($Q \propto t^0$) ordinary statistics is a consequence of the Gaussian central limit theorem. If the variances of *on* and *off* time distributions are finite ($\alpha > 2$), we expect that $P(w, t)$ will approach a Gaussian in the long time limit, hence, the photon counting statistics is ordinary (i.e., $p(n, t)$ is a Poisson transform

of a Gaussian, which means that photon statistics is essentially Poissonian). On the other hand, if the variances of *on* and *off* time distributions diverge, standard Gaussian behavior of $P(w, t)$ is not found even in the long time limit. Instead, as shown in Ref. [16] $P(w, t)$ will approach a Lévy stable law (with cut-offs and $1 < \alpha < 2$). Hence, $P(w, t)$ becomes very wide when $\alpha < 2$ and large fluctuations occur in the photon counts. This unusual fluctuation behavior in the photon counting statistics could be observed in the *ensemble* experiments as a signature of the power-law blinking kinetics in QDs or other chromophores.

IV. CONCLUDING REMARKS

Motivated by the power-law statistics in the spectral diffusion and blinking kinetics in QDs observed by the single QD spectroscopy, we have considered two related phenomena characterized by power-law stochastic processes: lineshape and photon counting statistics. By using the Kubo-Anderson oscillator model, we have generalized the stochastic lineshape theory to arbitrary renewal processes. Compared with the standard theory, we have found a variety of new phenomena in the lineshapes. Examples include new peaks not encountered in the usual KA model, and power-law narrowing behavior. The issue of the stationarity has been considered and the strong sensitivity of the lineshape to the first event in the stochastic trajectory was found, and it has been shown to be much more sensitive in the Lévy sojourn time PDF cases with diverging first moments ($0 < \alpha < 1$) than the cases with finite first moments.

In the second problem, we have considered the photon counting statistics of QDs undergoing fluorescence intermittency characterized by the power-law process, and showed that it exhibits unusually large fluctuations of photon number counts not encountered previously. The blinking kinetics has been mapped onto a Lévy walk process, and due to the long time tail in the sojourn time PDFs Mandel's Q parameter has been shown to increase in time even in the long time limit. This unusual fluctuation behavior in the photon counting statistics can be observed in the ensemble experiments as a signature of the power-law blinking kinetics in QDs or other chromophores. The time-dependent behavior of Q will yield information on the stochastic processes the individual QDs are undergoing.

Many dynamical processes in condensed phases usually hidden under ensemble averaging are now being revealed due to recent advances in single molecule spectroscopy [57–61], and some of them turn out to exhibit “strange kinetics” behavior, the subject to which this issue is devoted. Considering that many important systems under spectroscopic investigation show interesting, anomalous kinetic behavior, the present work or its variation will provide a useful theoretical framework to characterize

“strange” kinetic behavior of complex molecular systems in a “usual” way.

ACKNOWLEDGMENT

This work was supported by NSF. YJ and EB thank Ken Shimizu and Mouni G. Bawendi for useful discussions and Jean-Philippe Bouchaud for pointing out Ref. [49].

APPENDIX: PROBABILITY DENSITY FUNCTION FOR THE FIRST SOJOURN TIME

Although a derivation of the PDF for the first sojourn time given in Eq. (2.7) can be found in many places such as Refs. [42–45], we present its derivation here for the sake of completeness. We only derive the expression of $\psi_+(t_+)$ for simplicity. When calculating the PDF for the first transition event one can imagine large number of independent stochastic processes that have been going on for long times before $t = 0$ and have $+$ state at $t = 0$. In general, it is not known when each of ensemble has entered the $+$ state before $t = 0$, and we will call this time as $-t_0$. Now we define $\psi_+(t|t_0)$, the conditional probability density of the transition $+\rightarrow-$ occurring at time t knowing that a time t_0 has already elapsed since the last transition event to the $+$ state has been made. Then by making use of the definition of conditional probability we can write as

$$\psi_+(t|t_0) = \frac{\psi_+(t+t_0)}{\Psi_+(t_0)}. \quad (\text{A1})$$

In order to calculate the first transition event PDF $f_+(t)$, we have to average $\psi_+(t|t_0)$ over the density $\Psi_+(t_0)$,

$$f_+(t) = \frac{\int_0^\infty dt_0 \psi_+(t|t_0) \Psi_+(t_0)}{\int_0^\infty dt_0 \Psi_+(t_0)}. \quad (\text{A2})$$

With a simple change of variable it can be easily shown that

$$f_+(t) = \frac{1}{\tau_+} \int_t^\infty d\tau \psi_+(\tau), \quad (\text{A3})$$

which is Eq. (2.7).

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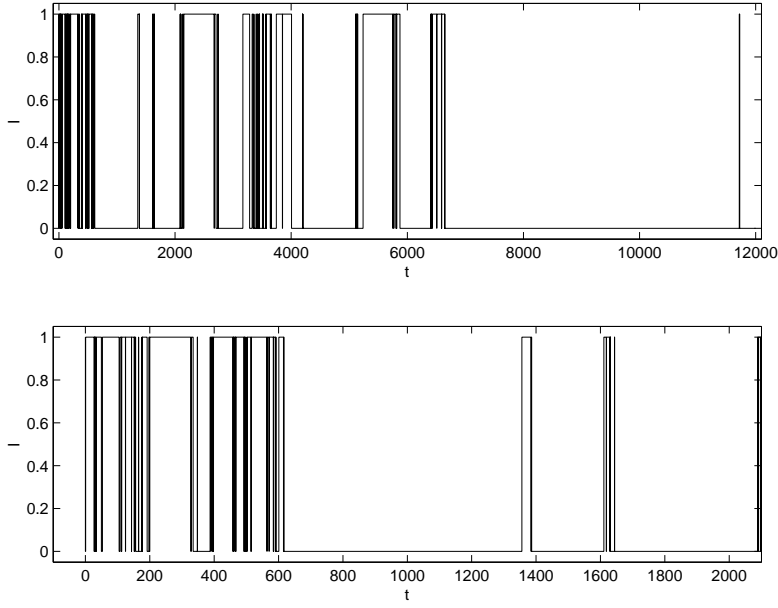


FIG. 1. A realization of the intensity fluctuation of a single QD obtained by using a two-state model. Intensity of the QD, $I(t)$, fluctuates between two states, $I_{\text{on}} = 1$ and $I_{\text{off}} = 0$. Statistics of *on* and *off* times are distributed with power-laws, $P_{\text{on(off)}}(t_{\text{on(off)}}) \sim t_{\text{on(off)}}^{-m_{\text{on(off)}}}$, and $m_{\text{on}} = m_{\text{off}} = 3/2$ were used to generate the trajectory. The lower panel is a zoom-in of the upper panel for $0 < t < 2100$. Note that two figures look similar on a different time scale, and in both figures long *off* times on the order of the total measurement time are observed ($6600 < t < 11700$ in the upper panel and $600 < t < 1370$ in the lower panel).

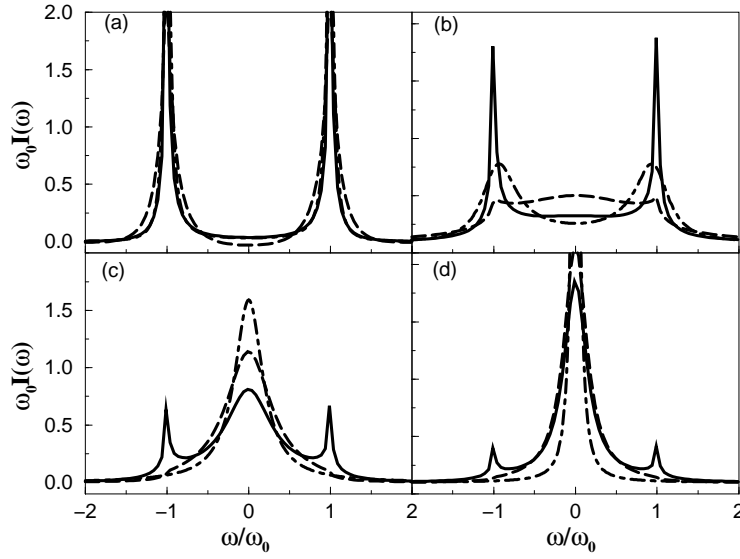


FIG. 2. The lineshapes calculated from $\psi_{3/2}(t)$ for the stationary, ($I(\omega)$, solid line) and the nonstationary ($\tilde{I}(\omega)$, dashed line) cases are compared with the KA case (dot-dashed line). The correlation time is chosen as $\omega_0\tau = 20, 4, 0.4$, and 0.08 in (a)-(d), respectively. The resonance frequency is chosen as $\omega_0 = 1$.

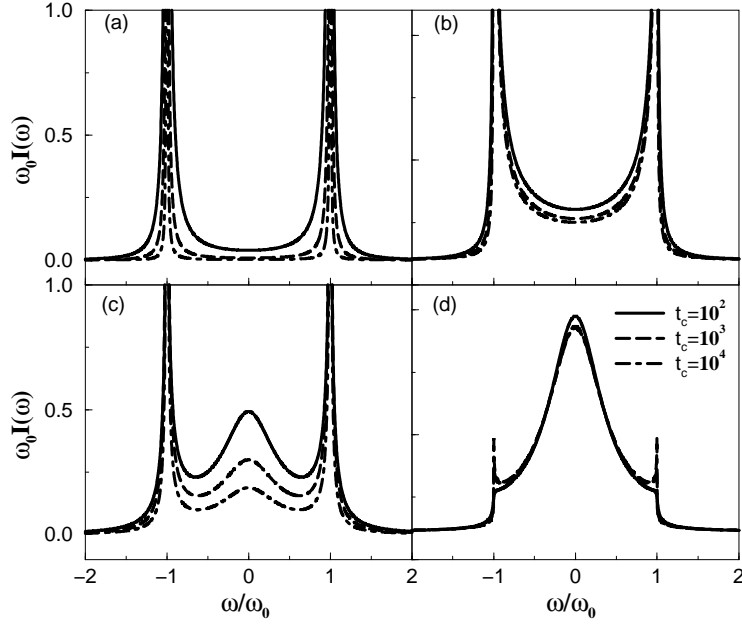


FIG. 3. The lineshapes are calculated with the Lévy PDF cases with two different values of the Lévy index, α and the cut-off time, t_c . $\alpha = 0.3$ case : (a) $I(\omega)$ (stationary) and (b) $\tilde{I}(\omega)$ (nonstationary). $\alpha = 0.8$ case : (c) $I(\omega)$ (stationary) (d) $\tilde{I}(\omega)$ (nonstationary). The other parameters are chosen as $\omega_0 = 1$ and $r_{\pm} = 1$.

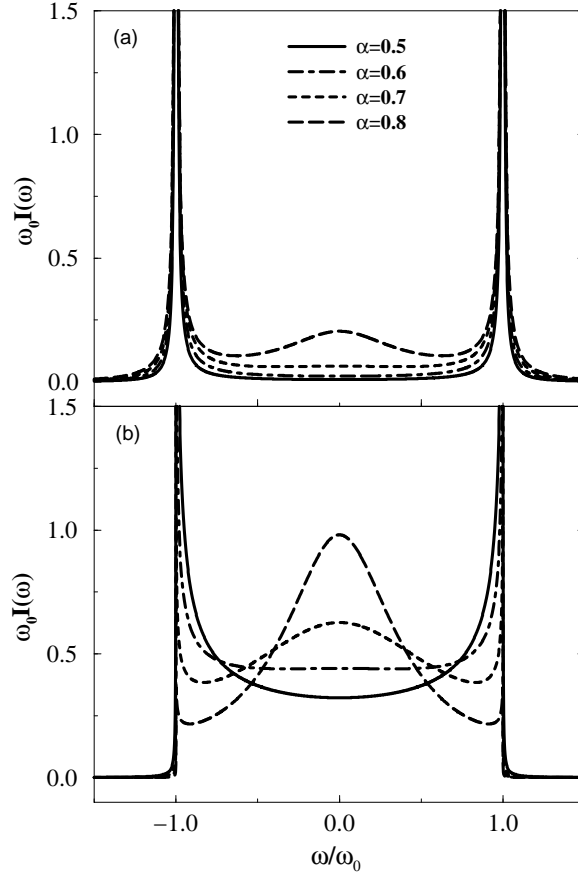


FIG. 4. The power-law narrowing behavior for the lineshape with Lévy PDF is shown as the Lévy index α is changed. (a) $I(\omega)$ (stationary case) and (b) $\tilde{I}(\omega)$ (nonstationary case). The other parameters are chosen as $r_{\pm} = 0.01$ and $t_c = 10^4$.